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MICELLES UNDER PRESSURE

By Henry W. Offen

The reported pressure effects on micelle formation, solubility and structure in aqueous solutions are reviewed. A number of ionic surfactants have been studied to establish the pressure dependence of micellization and to determine phase boundaries between micelles, singly dispersed surfactant, and hydrated solid. Other studies have focused on pressure perturbations of these polynuclear aggregates at the microscopic level. This review includes our recent results on micellar solubility and micellar size under pressure.

1. Introduction

Two comprehensive reviews on micelles listing over 400 references have recently been completed by Wennerström and Lindman¹⁾ and Lindman and Wennerström.²⁾ These attest to the recent explosion of basic knowledge about the interesting properties of these colloidal electrolytes. Proceedings of recent symposia on "micellization, solubilization and microemulsions" and on "solution chemistry of surfactants" have been published.^{3,4)} The effect of pressure on micelles received mention in only one sentence,²⁾ which reflects both the few pressure-related publications in the literature and the limited impact that pressure-related information has had in shaping the research frontiers in this important area of cooperative phenomena in aqueous solutions.

Amphiphilic molecules, consisting of a nonpolar (e.g. aliphatic hydrocarbon) group bonded to a polar or an ionic group and counterion, make up the important class of surfactants with their characteristic and unique properties.¹⁻¹²⁾ The most widely applicable solvent is water, to which all pressure work and this review is limited. Surfactants are classified into two groups: those which dissociate into ions in water and those which are neutral molecules, but with a strongly polar group aiding dissolution. The important properties of surfactants derive from their ability to aggregate spontaneously in aqueous solution above a certain concentration, called the critical micelle concentration (CMC).

It is known that the onset of micelle formation occurs over a concentration range, yet it is convenient and customary to refer to the CMC of a surfactant. Nearly all physical property-concentration plots for a surfactant-H₂O system exhibit relatively abrupt changes of slope in a narrow concentration range, labeled CMC. (The values of CMC are typically millimolar

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for ionic surfactants and micromolar for nonionics.) The CMC, as the most frequently measured property, has been studied as a function of alkyl chain length (straight paraffin chain), headgroup, counterion, the concentration of surfactant and electrolyte (with common ion), addition of solubilizers and solvent modifiers, temperature and pressure. Of these variables the pressure parameter has received the least attention. A typical ionic surfactant is sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4^-\text{Na}^+$); other types used in pressure work include the CO_2^- and $\text{N}(\text{CH}_3)_3^+$ headgroups and poly (oxyethylene)-type nonionic surfactants.

In addition to CMC- P studies, pressure research has concentrated on the phase equilibria of micelles, limited to low surfactant concentrations (less than a few percent in water), to temperatures near room temperature ($10\text{--}40^\circ\text{C}$), and to pressures generally below 2 kbar. The solubility curve and CMC curve divide surfactant- H_2O systems into three regions: singly dispersed or monomeric surfactant, singly dispersed plus association colloids called micelles and hydrated crystals. The effect of pressure has also been noted on the phase separation (two liquid phases) of nonionic surfactants at higher temperatures (the cloud point).

In order to understand the process of micellization, thermodynamic measurements must be augmented with techniques which focus on micellar structure¹⁻⁴⁾ and ion-water interactions.¹³⁻¹⁵⁾ The microscopic view of these organized temporal structures remains controversial.^{1,2,16)} About 10^2 monomers typically cluster to form ionic micelles with characteristic size, shape and interfacial properties. These colloidal particles derive their stability from a balance between hydrophobic and Coulombic interactions and ion hydration. The hydrocarbon part of the amphiphilic molecule resides in the interior of the micelle, while the headgroups along with water and counterions are crowded near the micellar surface.

2. Thermodynamics of Micellar Systems

2-1. Phase equilibria

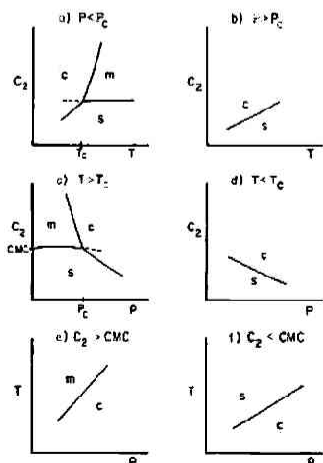


Fig. 1. Phase relationships of a typical ionic surfactant near CMC. The critical pressure P_c and critical temperature T_c (Krafft point) are defined as the point of intersection of the CMC and solubility curve; i.e., where singly dispersed solution, (s) micelle (m) solution and hydrated solid (c) are in equilibrium.

The behavior of aqueous surfactant solutions near the CMC may be discussed in terms of the phase diagrams shown in Fig. 1, which consider three phases (s, m and c), two components (solvent-1, surfactant-2) and three independent variables (P , T and surfactant concentration C_2). The three phases are singly dispersed surfactant (s), micellar aggregate in water (m) and hydrated solid (c). The solubility curve intersects the CMC curve at a critical point, akin to the triple point of a one-component system. The critical temperature T_c , here identified with the Krafft point, represents the point at which the slope of the solubility-temperature curve changes rapidly and at which the surfactant concentration is equal to the CMC. At the critical point, monomeric molecules, micelles and solid surfactant are in equilibrium in the solvent environment. The dotted lines in Figs. 1a and 1c indicate the fact that micelles are easily supercooled or superpressed.

Let us consider the equilibrium between a saturated solution of surfactant and the pure solid surfactant. The condition of equilibrium^{10,11)} is

$$\mu_2^c = \mu_2^s \quad (1)$$

Generally, the activity of the solid phase is considered constant and the expression for the solution of a uni-univalent electrolyte is written

$$\mu_2^s = \mu_2^\circ + 2RT \ln m_2 \quad (2)$$

in which m_2 is the saturation concentration or solubility, μ_2° is the chemical potential in a (hypothetical) standard state and the other symbols have their usual meaning.

The volume change ΔV^c describing the transfer of surfactant from solution to solid is {recalling $(\partial \mu / \partial P)_T = \bar{V}$ }

$$\Delta V^c = 2RT \left(- \frac{\partial \ln m_2}{\partial P} \right)_T \quad (3)$$

where ΔV^c is the difference in molar volume of the solid solute and the partial molal volume of solute in solution. Below the critical pressure P_c , \bar{V}^s is the appropriate substitution, while for $P > P_c$, the partial molal volume in the micellar phase (\bar{V}^m) must be used. Since the two differ in magnitude, the solubility curve will change slope as already discussed for the temperature dependence (Fig. 1).

2-2. Micelle formation

The above discussion (Fig. 1) has treated the formation of surfactant clusters as a phase separation. This so-called pseudo-phase separation model^{10,11,17-22)} has considerable appeal for pressure work, although it is only approximate and cannot address any questions relating to micellar structure. An alternate chemical equilibrium approach (mass-action model) has fewer shortcomings; however, it can be shown that with suitable approximations both approaches lead to identical equations within the framework of small-system thermodynamics.^{6,21)}

In this review, we will discuss the pressure work on micelle formation in terms of the

two-state, pseudo-phase separation model as one simple and useful perspective of the process of micellization. The CMC is here regarded as the saturation concentration of free amphiphile in solution relative to the micellar pseudo-phase.

The equations for the CMC- P curve of Fig. 1 can then be derived in parallel to those given above. Let us consider an aqueous system of surfactant and electrolyte with common counterion. (The addition of simple salts is commonly encountered in the study of micellar solutions.) The activity of the micellar pseudo-phase is equal to unity ($a_2^m=1$). If we neglect activity coefficient effects, a first approximation ($a_2=CMC$, $a_3=CMC+C_e$) is the equilibrium expression:

$$\Delta \bar{V}^m = RT \left[\frac{\partial \ln CMC}{\partial P} \right]_T + \beta RT \left[\frac{\partial \ln (CMC + C_e)}{\partial P} \right]_T \quad (4)$$

where $\Delta \bar{V}^m = \bar{V}^m - \bar{V}^l$, C_e =electrolyte concentration, and β is an empirical parameter, describing the fraction of counterions associated with the micellar aggregate (typically $0.4 < \beta < 0.7$).

In the absence of added salt ($C_e=0$), the equation most frequently quoted in pressure work is obtained:

$$\Delta \bar{V}^m = (1 + \beta) RT \left[\frac{\partial \ln CMC}{\partial P} \right]_T \quad (5)$$

The parameter β is assumed to be independent of pressure, which is not a bad approximation according to results presented later. If counterion binding is complete, $\beta=1$ and we have the expected factor of 2 for uni-univalent electrolytes. For nonionic surfactants β would equal zero.

The pressure derivative of the partial molar volume change on micelle formation leads to the isothermal partial molar compressibility change $\Delta \bar{K}^m$:

$$\Delta \bar{K}^m = - \left(\frac{\partial \Delta \bar{V}^m}{\partial P} \right)_T \quad (6)$$

Appropriate expressions for other extensive variables such as the enthalpy or entropy change can be derived in parallel fashion. As an example of the "multiple association equilibria" approach, the expression for the free energy change

$$\Delta G^m = (1 + \beta) RT \ln CMC \quad (7)$$

is obtained by substituting $\bar{v}=P/j$: where P is the average number of counterions bound by a micelle consisting of j monomeric surfactant molecules on the average. With respect to model testing, greater effort has gone into the critical assessment of thermodynamic quantities derived from their temperature dependence than into their pressure derivatives ($\Delta \bar{V}^m$ and $\Delta \bar{K}^m$), probably because thermal data are more abundant and accurate.

The $\Delta \bar{V}^m$ and $\Delta \bar{K}^m$ values obtained from the CMC vs. P curve can be compared with 1 atm measurements of the density and the speed of sound in the aqueous solution as a function of surfactant concentration (above and below CMC). Such measurements yield apparent partial

volumes ϕ_v and apparent, isentropic partial molal compressibilities $\phi_{K(S)}$.²³ Errors due to approximations required for comparison with Eqs. 5 and 6 tend to cancel because the difference in \bar{V} and \bar{K} is evaluated.

The reliability of the data diminishes, and only a few measurements exist, for the temperature derivative of pressure functions, *e. g.*

$$\left[\frac{\partial(J\bar{V}^m)}{\partial T} \right]_P = - \left[\frac{\partial(J\bar{S}^m)}{\partial P} \right]_T \quad (8)$$

where

$$J\bar{S}^m = J\bar{H}^m/T = - (1 + \beta) RT \left[\frac{\partial \ln \text{CMC}}{\partial T} \right]_P \quad (9)$$

Also, the $J\bar{V}^m$ and $J\bar{K}^m$ obtained at high pressures from CMC vs. P can be compared with direct measurements of volume and ultrasound speed as a function of pressure for surfactant solutions above and below the CMC.

In the study of homologous series of surfactants which differ only in the length of the alkyl chain, the measured $J\bar{V}^m$ have been dissected according to

$$J\bar{V}^m = J\bar{V}_{2a}^m + J\bar{V}_{2b}^m + \beta J\bar{V}_3^m \quad (10)$$

where $2a$ =micellar interior proportional to $(\text{CH}_2)_n$, $2b$ =surfactant headgroup, and 3 =bound counterion. In this manner the various contributions to the overall volume change upon aggregation may be estimated, albeit with great uncertainties.

The reader is reminded that aqueous solubility and clustering of electrolytes in water are complex properties for which a unified treatment is lacking and the framework for data analysis and correlation of pressure-dependent surfactant solution properties cannot realize the same measure of success as thermodynamic-microscopic correlations of better defined systems. The direct measurements²⁴ of thermodynamic functions over a wide range of concentration (down to at least 0.01 molal) provide standard comparisons with measurements of the effects of pressure, temperature and salt on the process of micellization.

3. Pressure Survey

Some thirty articles²⁵⁻⁵⁴ have been published in the period 1962-1980 (through May only) about the effects of high pressures on micelles in aqueous solution. Table 1 gives the names and abbreviations of surfactants used in high pressure research, including n -alkyl sulfates, carboxylates, substituted ammonium halides and polyoxyethylene-glycol monoethers. Universal agreement about abbreviations is lacking so that the conventions used in this review are arbitrary.

The various properties and experimental methods used to study them under pressure are listed in Table 2 (property symbols have been introduced in Section II). The thermodynamic

Table 1. Surfactants used in pressure experiments
(Abbreviations used in this review are listed in left column)

ANIONIC	
Alkyl Sulfates ($R_nOSO_3^-$)	
SOS	sodium octyl sulfate ($n=8$)
SDeS	sodium decyl sulfate ($n=10$)
SDS	sodium dodecyl sulfate (sodium lauryl sulfate)
STeS	sodium tetradecyl sulfate ($n=14$)
$R_{12}SO_4H$	dodecylhydrogensulfate
Alkyl Carboxylates (R_nCOO^-)	
R_nCONa – $R_{13}CONa$	
$R_{11}CONa$	sodium dodecanoate (sodium laurate)
$R_{11}COK$	potassium dodecanoate
$R_{11}CO(CH_3)_4N$	tetramethylammonium dodecanoate
CATIONIC	
Alkyl substituted ammonium or pyridinium halides	
DeTAB	decyltrimethylammonium bromide $R_{10}(CH_3)_3N^+Br^-$
DoTAB	dodecyltrimethylammonium bromide ($n=12$)
MyTAB	myristyltrimethylammonium bromide ($n=14$)
CTAB	cetyltrimethylammonium bromide ($n=16$)
DoAB	dodecylamine hydrobromide
DoAC	dodecylamine hydrochloride
DoTAC	dodecyl trimethylammonium chloride
DoBAC	dodecyl benzyltrimethylammonium chloride
DoPB	dodecyl pyridinium bromide
NONIONIC	
Polyoxyethylene dodecylether	
$C_{12}E_n$	$(CH_3)(CH_2)_{11}O(CH_2CH_2O)_nH$ $n=5, 6, 9, 14, 8, 19, 3, 23, 9$
Polyoxyethylene nonylphenyl ether	
PNE	$C_9H_{19}C_6H_4O(CH_2CH_2O)_{8-12}H$

Table 2. Pressure studies of micelles

Property	Method
CMC, ΔP^m , ΔR^m	conductivity (κ) absorbance (A)
\bar{V}^m , P^m	compression ($\Delta V/V$) ultrasound (u)
\bar{R}^m , R^m	ultrasound (u)
β	conductivity (κ) intensity light scattering (ILS)
Solubility	conductivity (κ) turbidity (τ)
Micellar Structure	conductivity (κ) T-jump (JT) intensity light scattering (ILS) photon correlation spectroscopy (PCS)

Table 3. Summary of pressure research with micelles

Reference	Surfactant System	P_{max} (bar) ^a	$T(^{\circ}C)^b$	Method	Property
(25)	SDS	2000	25	κ	CMC, $\Delta \bar{V}^{\circ}$
(26)	R_nMe_3NBr ($n=8, 10, 12$) DoTAB plus Phenol	3000	25	κ	CMC
(27)	DoAC, DoTAC, DoBAC	5000	25	κ	CMC, $\Delta \bar{V}^{\circ}$
(28)	DoAC	2000	25	τ	solubility
(29)	R_nOSO_3Na , R_nMe_3NBr ($n=10, 12, 14$) PNE	3000	7-40	κ, τ	CMC, $\Delta \bar{V}^{\circ}(P, T)$, $\Delta \bar{S}^{\circ}$, solubility
(30)	DoBAC	5000	25-45	κ	CMC, $\Delta \bar{V}^{\circ}(P, T)$, $\Delta \bar{S}^{\circ}$
(31)	PNE	5000	30-70	τ	cloud point
(32)	SDS, DoAB	3000	7-35	κ	solubility, CMC
(33)	SDS	4000	230	HPLC ^c	m-s equilibrium
(34)	R_nOSO_3Na ($n=8, 10, 12$) R_nMe_3NBr ($n=10, 12$)	2000	25	$\Delta \bar{V}/\bar{V}, \kappa$	$\bar{V}^{\circ}, \bar{V}^{\circ}, CMC, \Delta \bar{V}^{\circ}$
(35)	R_nOSO_3Na ($n=8, 10, 12, 14$)	3000	17-40	κ	CMC, β , $\Delta \bar{V}^{\circ}(P, T)$, $\Delta \bar{S}^{\circ}$
(36)	DoTAB plus urea	2500	25, 35	κ	CMC, $\Delta \bar{V}^{\circ}$
(37)	SDS plus naphthalene	5500	25	A	CMC
(38)	CTAB	2500	25	κ	CMC, solubility
(39)	DeTAB, DoTAB, MyTAB	2500	25	κ	CMC, β , solubility
(40)	SDS	2000	25, 40	κ	CMC
(41)	R_nOCOM ($M=Na, K, Me_4N$), SDS	1600	25	κ	CMC, $\Delta \bar{V}^{\circ}$, $\Delta \bar{R}^{\circ}$
(42)	R_nOCONa	1600	25	κ	β
(43)	R_nOCONa plus NaCl	1600	25	κ	CMC, $\Delta \bar{V}^{\circ}$, $\Delta \bar{R}^{\circ}$
(44)	R_nOCONa ($n=6-11, 13$)	1600	25	κ	CMC, $\Delta \bar{V}^{\circ}$, $\Delta \bar{R}^{\circ}$
(45)	R_1SO_4H	3000	40	κ	CMC
(46)	SDS	700	21-25	JT	relaxation time
(47)	$C_{12}E_8$ ($n=5, 6$) plus hexane, octane	1500	24-60	τ	cloud point
(48)	$R_{12}SO_4H$	2000	40	k^d	catalysis
(49)	R_nOCONa	1600	10-40	u	$\bar{V}^{\circ}(P \text{ or } T), \bar{V}^{\circ}(P \text{ or } T)$, $\bar{K}^{\circ}(P \text{ or } T), \bar{K}^{\circ}(P \text{ or } T)$
(50)	MyTAB	3000	12-41	PCS	R_g
(51)	SDS plus naphthalene	3000	30	κ	CMC
(52)	$C_{12}E_8$ ($n=6, 9, 14, 8, 19, 3, 23, 9$)	1600	25	$\Delta \bar{V}/\bar{V}$	$\bar{V}^{\circ}, \bar{K}^{\circ}$
(53)	SDS, $C_{12}E_8$	1400	25, 30	ILS	j^f, C_m, β
(54)	DoPB	2000	30	A, κ	CMC

a. The maximum pressure reported for most experiments.

b. The temperature or temperature extremes at which some pressure runs were reported.

c. HPLC=high pressure liquid chromatography.

d. k =rate constant.e. R_g =average hydrodynamic radius of micelles.f. i =average aggregation number.g. C_m =micelle concentration.

properties of micelle formation and phase stabilities have received the most attention, while the modification of micellar structure (microscopic properties) under pressure is receiving increasing attention. The principal methods in use are electrical conductivity, liquid volume compression, sound velocities and light scattering.

In Table 3 is found a chronological overview (Refs. 25-54) of surfactant system, pressure and temperature regime, and method and property studied under pressure. Pressures are given in units of bar, although atm, kg cm^{-2} , MPa or psi may have been used in the research papers ($1 \text{ kbar} = 1000 \text{ bar} = 100 \text{ MPa} = 986.9 \text{ atm} = 1019.7 \text{ kg cm}^{-2} = 14\,501 \text{ psi}$). There are only few laboratories in the world which focus on surfactant aggregation at high pressures, foremost among these are the continuing contributions from the laboratory of Professor M. Tanaka and his collaborators. Specific recognition is given his first comprehensive report²⁹⁾ published in 1968 (in Japanese), which formed the foundation for many of his later articles. Secondly, one comprehensive thermodynamic study of alkyl carboxylates (chain length, counterion, β , electrolyte concentration) has been completed by Dr. E. Vikingstad⁵⁵⁾ in conjunction with Professor Høiland; their pressure work led to five publications in 1978-79.

Inspection of Table 3 reveals, not unexpectedly, that the one universal property of micelles, the CMC, has also received the most frequent attention from pressure researchers. The conductivity method is a reliable (at pressure as well as under normal conditions) means for detecting the CMC of ionic micelles. (The accuracy deteriorates somewhat at high ionic strength.) If the specific conductivity κ is plotted for a series of surfactant concentrations C_2 , the κ vs C_2 plots consist of two lines of different slope, the break identified as the CMC. κ is measured for each solution at definite pressure intervals^{25-27,29,30,32,34-36,38-41,43-45,51,54)} from which CMC vs. P plots and polynomial expansions in powers of P can be extracted. The volume change for micellization $\Delta \bar{V}^m$ can be obtained as the slope at any pressure according to Eq. 5. If the surfactant molecule contains a chromophore which is sensitive to aggregation then visible/ultraviolet absorption can be monitored as a function of pressure for a series of solutions.⁵⁴⁾ The addition of a solubilize has also been used to find the onset of micelle formation by differential absorption spectroscopy.³⁷⁾

The evaluation of $\Delta \bar{V}^m$ according to Eq. 5 requires knowledge of the value of β , the fraction of counterions bound to the micelle. Generally, the β parameter in Eq. 5 is identified with the slope of $\log \text{CMC}$ vs. $\log (\text{CMC} + C_1)$ plots. Here C_1 is the concentration of simple, inorganic salts, with a common ion between electrolyte and surfactant, added to the micellar solution. These plots can be prepared for each pressure and a $\beta(P)$ functional behavior is obtained.^{35,39,42)} Light scattering is another method which has recently been exploited to estimate the net charge on micelles in compressed solution.⁵³⁾

The pressure dependence of the partial molal volume of surfactant in the singly dispersed (\bar{V}^1) and micellar (\bar{V}^m) states is found by measuring the bulk compression ($\Delta \bar{V}/\bar{V}$)^{34,52)} or the speed of sound⁴⁹⁾. The latter method is probably more accurate, especially when partial molal compressibilities \bar{K} are desired.

The phase diagram of ionic surfactants (Fig. 1) and nonionics has been explored with the pressure parameter. Solubility measurements are particularly difficult because of the question of equilibrium attainment. As in the case of CMC, the electrical conductance of the solution is the most often used technique to study the saturation solubility and the Krafft temperature of ionic micelles under pressure^{29,32,38,39}. The nonionic surface active agents have the interesting property that isotropic micellar solutions turn cloudy as the temperature is raised (the cloud point). The monitoring of the turbidity of the solution as a function of pressure yields the pressure behavior of the cloud point.^{28,29,31,47} The change in turbidity can also be used to detect crystal formation or dissolution of ionic surfactants.²⁸

The methods discussed so far provide little insight into the size, shape and polydispersity (size distribution) of micelles. Micellar structure is a current topic of controversy, and the pressure dependence of micelles at the microscopic level will be one additional input to sort out the various forces responsible for surfactant clustering. Photon correlation spectroscopy⁵⁶⁻⁵⁸ (PCS), also called quasi-elastic light scattering, has been used to measure the pressure dependence of the effective hydrodynamic radius of cationic surfactant micelles^{50,59}. Intensity or classical light scattering (ILS) techniques have also recently been applied to pressure studies of the aggregation number j and the concentration of micelles C_m ⁵³. Both techniques are restricted to average molecular properties, and further experimental advances are necessary to study the shape and size distribution of micelles in solution.

The remainder of this review presents the results of pressure studies under the headings of micellization, phase equilibria and micelle structure. Two studies which do not easily fit those three categories are briefly mentioned here. First, SDS adsorption from a high pressure aqueous fluid at high temperatures and in the presence of 0.1 M electrolyte leads to micelle dissociation above ~ 2 kbar.³³ Second, the pressure effect on the micelle catalyzed hydrolysis of various alkyl acetate esters has been observed at 40°C.⁴⁸ The pressure modification of the reaction rate is greatest for the longest alkyl ($n=4$) chain studied; the rate vs. P curve has a pronounced minimum near 1 kbar (except for the methyl group) which is identified with micellar properties. Micellar catalysis at high pressures provides another important avenue for studies of solubilization mechanisms which may find increasing attention in these colloidal electrolyte solutions.

4. Micellization

One of the preferred means of determining micellar stability is the direct measurement of the volume and compressibility as a function of pressure and/or temperature for surfactant solutions above and below the CMC. Vikingstad, Skauge and Høiland⁴⁹ made such a study for sodium decanoate ($R_9\text{CONa}$) and their results are shown in Table 4. These are the results, which may be considered typical for anionic surfactants:

- * the apparent molal volume of ions increases with pressure, but the compressibility

Table 4. Thermodynamic quantities for R_9OCONa (adapted from Ref. 49)

	ϕ_V^a	ϕ_V^b	$\Delta \bar{V}^m$ ^b	$\Delta \bar{V}^m$ ^c	$\phi_{K(s)}^d$	$\phi_{K(s)}^d$	$\Delta \bar{K}^m$
Pressure ($T=25^\circ\text{C}$)							
1	165.4	175.0	9.6	9.5	-63	51	114
400	167.2	173.1	5.9	5.8	-37	27	64
800	168.6	172.0	3.4	3.0	-22	13	35
1200	169.3	170.3	1.0 ± 1.0	0	-11	6	17
1600	169.8	169.3	-0.5 ± 1.0	-1.0	-4	4	8
Temperature ($P=1$ bar)							
			$\Delta \bar{V}^m$ ^f				
10	160.2	171.9	11.7		-99	38	137
20	163.9	173.9	10.0		-76	47	123
30	166.8	175.8	9.0		-50	55	105
40	169.3	177.7	8.4		-28	63	91

- a. ϕ_V is the symbol for apparent molal volume, uncertainty is $\pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ for both ϕ_V and ϕ_V^b .
- b. $\Delta \bar{V}^m$ is calculated from ultrasound determinations; error is $\pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$.
- c. $\Delta \bar{V}^m$ evaluated by Eq. 5 from conductivity measurements; error is $\pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$.
- d. the uncertainty in the apparent, isentropic molal compressibility is $\pm 3 \times 10^{-4} \text{ cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$ for both $\phi_{K(s)}^d$ and $\phi_{K(s)}^d$.
- e. errors are $\pm 5 \times 10^{-4} \text{ cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$.
- f. $\Delta \bar{V}^m$ from density measurements ($\pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$).

becomes rapidly less negative with increasing pressure;

* the apparent molal volume of micelles decreases upon compression with a reduced rate at the higher pressures;

* the difference between the above, $\Delta \bar{V}^m$, is positive at 1 bar and decreases with pressure; $\Delta \bar{V}^m$ is zero around 1200-1400 bar and negative above that pressure; the change in compressibility $\Delta \bar{K}^m$ is cut nearly in half for every 400 bar interval;

* raising the temperature above 25°C increases both singly dispersed and micellar volumes, but at differing rates, such that $\Delta \bar{V}^m$ and $\Delta \bar{K}^m$ are reduced at elevated temperatures.

The $\Delta \bar{V}^m$ and $\Delta \bar{K}^m$ (at 25°C and 1 bar) for the homologous series of alkyl carboxylates has been determined in the same laboratory.^{41,43,44} Some of their data is reproduced in Table 5 to support the following conclusions:

- * an increase in hydrocarbon chainlength increases both $\Delta \bar{V}^m$ and $\Delta \bar{K}^m$;
- * electrolyte addition reduces $\Delta \bar{V}^m$ and, to lesser degree, $\Delta \bar{K}^m$;
- * replacing the Na^+ counterion with K^+ has negligible effect, but the tetramethylammonium cation reduces both $\Delta \bar{V}^m$ and $\Delta \bar{K}^m$ appreciably;
- * the agreement between $\Delta \bar{V}^m$ and $\Delta \bar{K}^m$ values from density measurements and from the pressure dependence of CMC is excellent, supporting the applicability of Eq. 5 from the phase separation model.

The alkyl sulfates, which comprise the other class of anionic surfactants studied under pressure, follow the same trends as reported above with respect to temperature, salt and

Table 5. Thermodynamic quantities for alkyl carboxylates at 25°C and 1 bar (adapted from Refs. 41, 43, and 44)

Surfactant	$\Delta\bar{V}^m$ ($\leq \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$)	$\Delta\bar{V}^m$ ^b	$\Delta\bar{K}^m$ ($\pm 5 \times 10^{-4} \text{ cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$)	$\Delta\bar{K}^m$ ^d
R ₇ OCO Na	8.9	8.6	92	104
R ₈ OCO Na	9.2	8.8	102	112
R ₉ OCO Na	9.6	9.5	114	115
R ₁₀ OCO Na	10.2	10.2	124	127
R ₁₁ OCO Na	11.2	10.8	139	135
R ₁₁ OCO Na + 0.08m NaCl	10.0	10.1	132	120
R ₁₁ OCO K	11.1	10.5	140	150
R ₁₁ OCO Me ₄ N	7.8	8.2	117	110

a. By density measurements.

b. Calculated with Eq. 5.

c. By ultrasound measurements.

d. Calculated with Eq. 6.

Table 6. Thermodynamic quantities for sodium dodecyl sulfate (SDS) (taken from Refs. 29 and 35)

		$\Delta\bar{V}^m$ (Eq. 5)	$\Delta\bar{S}^m$ (Eq. 9)
$P < P_{max}$	$T < T_{min}^b$	+	+
	$T > T_{min}$	+	-
$P > P_{max}$	$T < T_{min}$	-	+
	$T > T_{min}$	-	-

a. $P_{max} \sim 1200$ bar represents the maximum in the CMC vs. P curve (see Fig. 1).b. $T_{min} \sim 20-25^\circ\text{C}$ represents the minimum in the CMC vs. T plot (see Fig. 1).

hydrocarbon chainlength. Kaneshina *et al.*³⁵⁾ studied the micellization process of SDS as a function of P and T and classified the thermodynamic quantities $\Delta\bar{V}^m$ and $\Delta\bar{S}^m$ according to sign into four groups, as shown in Table 6. Cross derivatives of thermodynamic quantities, e. g. Eq. 8, have been evaluated.^{29, 35, 36, 49)} The results are $\partial\Delta\bar{V}^m/\partial T < 0$ ($\partial\bar{V}^1/\partial T > \partial\bar{V}^m/\partial T > 0$) and hence $\partial\Delta\bar{S}^m/\partial P > 0$ ($\partial\bar{S}^1/\partial P < \partial\bar{S}^m/\partial P < 0$).

As evident from Table 3, the pressure dependence of the CMC has been most frequently investigated. Hamann²⁵⁾ published the first paper on CMC vs. P in 1962; some 18 publications have dealt with this subject since. The $\Delta\bar{V}^m$ values at 1 bar obtained from CMC vs. P plots and using Eq. 5 (or equivalent expression) are summarized in Table 7. The general features of the observations are:

* the pressure effect, akin to the temperature dependence of the CMC, is generally small

Table 7. The volume change for micelle formation, ΔV^m , derived from pressure research^a

Surfactant	T (°C)	ΔV^m ^b (cm ³ mol ⁻¹)	Reference
SOS	35	4.9	(35)
SDeS	35	7.9	(35)
SDS	35	10	(35)
STeS	35	11.3	(35)
SDeS	25	8.0	(34)
SDS	25	11	(25, 40)
	25	10.1	(41)
	40	7	(40)
SDS+naphthalene	30	7.5	(51)
DeTAB	25	3.9	(39)
	25	4.6	(34)
DoTAB	25	4.1	(39)
	25	3.3	(27)
MyTAB	25	8.2	(39)
CTAB	25	10	(38)
DoTAB+6M urea	25	1.5	(36)
DoAC	25	2.6	(27)
DoTAC	25	2.9	(27)
DoBAC	25	4.4	(27)
	25	4.5	(30)
	35	0.6	(30)
	45	-2.3	(30)

a. See Table 5 for ΔV^m of alkyl carboxylates.b. The ΔV^m probably have errors of ± 1 cm³ mol⁻¹.(i. e., $\Delta V^m < 11$ cm³ mol⁻¹ for alkyl chainlengths $n \leq 16$):

* the pressure effect on cationic surfactants is smaller than for anionics with the same hydrocarbon core size;

* the trends in pressure behavior of cationic surfactants differ markedly from those measured for alkyl carboxylates and sulfates discussed above.

Fewer detailed studies of cationic surfactants are available, but in support of the last point, several observations can be made. As noted in Table 7, the ΔV^m of anionic surfactants exhibit only a small decrease at elevated temperature, while DoBAC (the only cationic studied as a function of T and P) shows a large temperature dependence. Osugi, Sato and Ifuku³⁰ find that the maximum in the CMC vs. P curve actually disappears above 35°C. This result is the exception to the generalization of the existence of a maximum in the CMC vs. P curve of micellar aggregates (the surfactant DoAC at room temperature also does not show a maximum,²⁷ perhaps due to solubility problems). Another difference in the thermodynamics of micellization of the two classes of ionic micelles is evident from the fact that ΔV^m values determined as a

Table 8. Compression of Surfactant Solutions (adapted from Ref. 34)

Surfactant	$\bar{V}^s(1 \text{ bar})$	$\bar{V}^s(2000 \text{ bar})$	$\bar{V}^m(1 \text{ bar})$	$\bar{V}^m(20000 \text{ bar})$
SOS	172.6	176.7	178.0	171.4
SDeS	204.1	205.5	212.5	202.7
DeTAB	255.4	248.7	262.3	245.7

function of pressure both by compression (fractional volume change) and by conductivity measurements are in agreement with density determinations at 1 bar for anionic surfactants but not for cationics³⁴; e. g., the $\Delta\bar{V}^m$ for DeTAB is 2.3 cm³mol⁻¹ smaller by CMC vs. P determinations than by density measurements.³⁴ A third difference between cationic and anionic micelles is the pressure dependence of the singly dispersed surfactant volume (\bar{V}^s). Table 8 demonstrates that surfactant systems with counter-cations show a volume increase upon compression, while cationic amphiphiles shrink with increasing pressure.

The $\Delta\bar{V}^m$ values in Table 7 have been exclusively determined by conductivity measurements. We made an attempt to measure the CMC vs. P curve of SDS at 25°C by differential absorbance techniques on solubilized naphthalene and failed to observe a pressure maximum.³⁷ Recent conductivity measurements at 30°C for SDS plus saturated naphthalene solutions, however, found the behavior of SDS micelles to be independent of the presence of naphthalene.⁵¹ Therefore, our conclusion derived from probe absorption is likely to be erroneous; the probable explanation is that impurities (fourth component) such as dodecanol modified the pressure behavior of the SDS-naphthalene system. This would explain the low CMC value reported by us relative to that of Taniguchi and Suzuki⁵¹ for the SDS-saturated naphthalene system.

High concentrations of urea³⁶ or phenol²⁸ additives reduce the pressure response of DoTAB appreciably. Urea raises the CMC, while phenol lowers it, yet both exhibit diminished $\ln\text{CMC}/dP$. The behavior of surfactants with added organic material or salt appears to be largely determined by effects on the monomeric surfactant rather than on the colloidal particles.^{34, 43, 60}

In studies of homologous series it is sometimes customary to seek correlations as expressed by Eq. 10^{61, 62}. Kaneshina *et al.*³⁵ have done so for alkyl sulfates by ignoring the third term (counterion contribution) and conclude that the observed decrease in $\Delta\bar{V}^m$ with pressure is due to an increase in $\Delta\bar{V}^s$ (headgroup ion) and a decrease in $\Delta\bar{V}^m$ (hydrophobic chain). Vikingsd., Skauge and Høiland⁴⁴ suggest for alkyl carboxylates that $\Delta\bar{V}^m$ is not linearly dependent on chainlength and that the contribution from the counterion binding must be included to explain the $\Delta\bar{V}^m$ increment observed when adding a methylene group to the hydrophobic solute. This conclusion has also been supported by other recent studies at atmospheric pressure.^{63, 64}

The reported results on the pressure-dependence of micellization have not been assimilated into a theoretical model; in fact, the qualitative statements made about the driving forces responsible for pressure-induced shifts in micellar stability are sometimes in doubt when

scrutinized over a large P , T , C_2 regime. The direct measurement of volume and compressibility verifies that the monotonic decrease in $\Delta\bar{V}^m$ with increasing pressure is due to the higher compressibility of the micelles relative to monomeric amphiphilic molecules. The difference in $\bar{V}^l(P, T)$ and $\bar{V}^m(P, T)$, as well as in $\bar{K}^l(P, T)$ and $\bar{K}^m(P, T)$ determine the observed pressure perturbations on micelle formation; these are discussed in terms of the forces held responsible for aggregation up to some average, finite number of amphiphile units.

Micellar stability is achieved by a delicate balance between hydrophobic interactions (primarily entropic in origin and arising from changes in water structure upon dissolution of hydrophobic solutes) and electrostatic repulsions between hydrated head and between charged micelles mitigated by counterion binding and salt addition, respectively. The observed pressure modifications are then attributed to a shift in the hydrophobic and hydrophilic hydration of aggregate relative to monomer. For example, if pressure is observed to inhibit micelle formation, reduced hydrophobic hydration—pressure breaks up water structure—may be given as the principal reason. The different P , T response of cationic surfactants relative to anionics is probably due to the weaker hydration of counter-anions. While the partitioning between the two kinds of hydration may not be clearly assignable, the importance of modifications in water structure is well established and attains greater significance in comparison with other research on micelles.¹⁻⁴⁾

One chief conclusion from thermodynamic measurements of micellar properties relates to the nature of the micellar nucleus (the 'inner' hydrocarbon core). Partial molal volumes and compressibilities of alkanes in micellar aggregates resemble the partial molal quantities of liquid alkanes.^{41,45,60)} This result suggests that the interior of micelles is liquid-like, in agreement with inferences from other studies,^{1-4,7)} and confirms the expected site of solubilization of alkanes.

5. Phase Equilibria

Although the temperature dependence of surfactant solubilities in water was frequently studied in the early years of detergency, the same cannot be said for the pressure effect: in fact solubility studies of ionic surfactants under pressure have been limited to four amphiphiles: SDS^{24,32)}, DoAC,^{27,28)} DoAB³²⁾ and CTAB.³⁸⁾ Difficulties in confirming the equilibrium saturation line are equally encountered in both temperature and pressure determinations, *i. e.* consideration must be given to the existence of supercooled or superpressed micelles in aqueous solutions.

Osugi, Sato and Ifuku²⁷⁾ had the first encounter with precipitation-dissolution and the associated hysteresis for the cationic surfactant DoAC, which is characterized by a rather low solubility. Hysteresis is an indication of a phase separation, similar to the freezing and melting of one-component systems.⁶⁷⁾ Hamann²⁸⁾ demonstrated the large irreversibility of the m-c (micelle-hydrated solid) phase transition of DoAC in water by optical observation of the

freezing and dissolution process. In light of the problems associated with distinguishing between thermodynamic and kinetic stabilities the apparent solubilities of surfactants are frequently only measured. The general shape of the apparent solubility curve mirrors the equilibrium curve as in the case of CTAB³⁸⁾ with $P_c \sim 1600$ bar, *i. e.* a large decrease in apparent solubility for $P < P_c$ followed by a more gradual decrease for $P > P_c$.

The phase relationships of SDS^{29,32)} and DoAB³²⁾ have been studied in greater detail by Tanaka and his collaborators and led them to construct a three-dimensional phase diagram.³⁹⁾ The saturation curve is obtained by identifying the intersection of the upstroke and downstroke value of the specific conductivity for several concentrations and at several temperatures bracketing T_c . From this data $\log m_2$ vs. P plots are constructed at different temperatures. Below T_c , $d \log m_2 / dP$ is small and negative (*i. e.* solubility decreases slowly); above T_c , its pressure dependence is large for $P < P_c$ and again small for $P > P_c$. The critical temperature T_c rises linearly with increasing pressure (Fig. 1e). The critical behavior of MyTAB shows similar trends.⁵⁰⁾

The evaluation of ΔV° (Eq. 3) from the pressure dependence of the solubility curve does not inspire the same degree of confidence as the use of Eq. 5 for CMC vs. P plots, and in fact, ΔV° values have not been tabulated. But it is clear that ΔV° is large and negative, in contrast to ΔV^m which is small and positive at 1 atm (Fig. 1). Further, comparison of SDS and DoAB (same hydrocarbon chainlength) shows that the pressure-induced phase separation occurs at much lower pressures for DoAB than for SDS.³²⁾ The available pressure data on aqueous solubilities of surfactants cannot be analyzed beyond the above general statements.

Some preliminary work from my laboratory on micellar solubilities is shown in Figs. 2 and

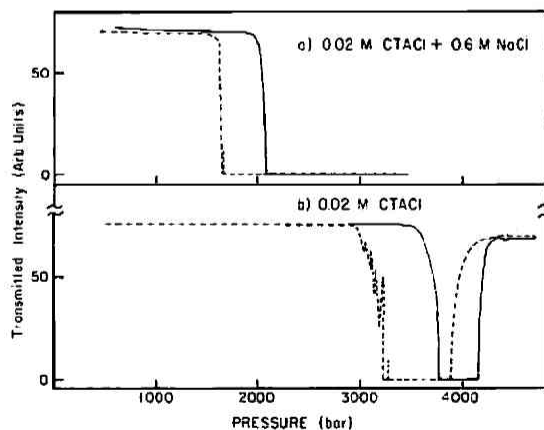


Fig. 2. The pressure dependence of the transmitted light for two micellar solutions at 32.0°C. The m-c phase transition is indicated by a large change in light intensity. Solid lines represent the upstroke behavior while dashed lines indicate the downstroke dependence.

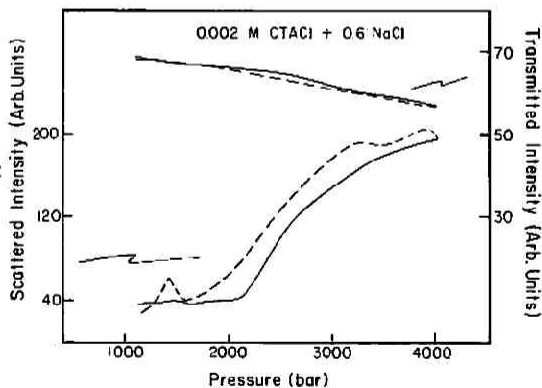


Fig. 3. The pressure dependence of the transmitted and scattered light at 32.0°C for 0.002 M CTACl plus 0.6 M NaCl. The solid line represents increasing pressure and the dashed line indicates decompression for the same run.

3. The transmitted and scattered light from cetyltrimethylammonium chloride (CTACl) solutions has been monitored as the pressure is slowly changed at 32.0°C with an apparatus described elsewhere.⁶⁹ (In that publication, the results for the freezing and melting of benzene also are illustrated.) Figure 2 compares the location and hysteresis of the phase transition of CTACl in the absence and presence of high salt concentration, with the surfactant concentration being about $10 \times \text{CMC}$ in the absence of electrolyte. The change in transmitted light intensity upon freezing or dissolution occurs at much higher pressure and with a larger zone of indifference in the absence of NaCl. Figure 2b indicates the macroscopic fluctuations observed upon dissolving the crystalline suspension. Also, the appearance of a third phase at higher pressures, characterized by a smaller hysteresis width, is indicated in Fig. 2b. The identity of this phase is not known, but lyotropic mesomorphism^{69,70} is commonly encountered at higher concentrations and liquid crystalline phases could become stabilized at high pressures. As the concentration of surfactant is lowered, the change in turbidity is best observed at 90° to the laser light input (see Fig. 3). Comparison of Figs. 2a and 3 show the effect of reducing the surfactant concentration tenfold: the onset of the transition occurs at slightly higher pressure and salting out effect is not as distinct, occurring over a wider pressure range. The mechanism of getting from micelle to crystallite and *vice versa* is unclear, but light scattering is a promising technique for uncovering the details of packing rearrangements of solutes in the presence of solvent, the major component of the system. However, it has been demonstrated^{50,59} that growth in micelle size is not a prerequisite for precipitation.

A few studies have been reported on the pressure response of nonionic surfactants.^{31,47,52} While the CMC vs. P curve has not been investigated, another aspect of phase stability, peculiar to nonionics, has been investigated by optical methods. This interesting feature is a phase transition as the solution temperature is raised. The separation into two liquid phases (one richer in surfactant than the other) is easily observed by turbidity measurements. The temperature of the equilibrium phase boundary, appropriately called the cloud temperature, increases with increasing pressure. PNE shows a maximum in the cloud point vs. P curve near 1500 bar³¹ while C_{12}E_3 and C_{12}E_6 surfactants exhibit a monotonic increase up to 1500 bar at a rate of $\sim 100 \text{ bar K}^{-1}$.⁴⁷ The addition of hexane or octane solubilizate had little effect on the slope.⁴⁷

The compression of C_{12}E_6 micellar solutions is linear in pressure and its magnitude of $\sim 5\%$ near 1400 bar is similar to that observed for ionic micells.²⁵ The apparent molal compressibility is observed to decrease as the hydrophilic oxyethylene chain is lengthened.⁵² Hydrogen bonding of the oxyethylene groups is a major driving force in nonionic surfactant systems. The observed results are in agreement with the generalization that the initial application of pressure strengthens H-bonds and weakens hydrophobic interactions.^{71,72}

6. Micelle Structure

This review has emphasized reported facts and minimized discussions of various qualitative interpretations put forward in the literature. In considering the influence of pressure on the microscopic structure of micelles, even greater caution is required, because several assumptions are generally required to go from data to interpretation. As Menger aptly remarked in his review¹⁶⁾: micelles have managed to elude detailed understanding despite the large number of published results. This conclusion applies equally well to pressure work on micelle structure, so far limited to counterion binding, aggregation number and micelle radius.

One important quantity of micellar structure is the degree of counterion binding. The parameter β is defined as the ratio of counterion to amphiphile associated with the micelle, even though the distinction between counterions differing in radial distance from the micelle core is at best ambiguous. Most experimental determinations of the pressure effect on β have used conductivity measurements in surfactant-salt systems:

$$\log \text{CMC} = -\beta \log(\text{CMC} + C_s) + \text{constant} \quad (T, P) \quad (11)$$

Although β is not directly related to the slope of the CMC vs. $\ln(\text{CMC} + C_s)$ plots,²⁾ the validity of Eq. 11 has been assumed in order to evaluate $\beta(P)$. The values obtained at 1 atm in this way are in good agreement with emf measurements for alkyl carboxylates,⁴²⁾ perhaps because β is observed to be a rather insensitive quantity relative to most parameters, in analogy to ion condensation phenomena in other polyelectrolyte systems.⁷³⁾ Similar pressure insensitivity is found for counterion association, at least below 3000 bar. Sodium dodecanoate⁴²⁾ at 25°C shows first a slight decline in β at low pressure, then a small increase to 1600 bar. The cationics DeTAB and DoTAB³⁹⁾ at 25°C show β to be pressure-independent up to 1500 bar, followed by a small increase to 2500–3000 bar. A stronger pressure effect was reported for β of SDS at 35°C, evaluated by Eq. 11 at different pressures,³⁵⁾ but this was not verified by light scattering measurements³³⁾ of SDS at 30°C, which suggest that the β parameter is pressure-independent.

Nishikido, *et al.*⁵³⁾ have recently reported the effect of pressure on the average aggregation number j of SDS at 30°C and C₁₂E₆ at 25°C, as determined from Debye plots of scattered light intensities. The j of SDS micelles (for $C_2 \sim 4 \times \text{CMC}$) change from ~ 60 ($P = 1$ atm) to ~ 30 ($P_{\text{min}} \sim 1000$ bar) and then to ~ 70 ($P \sim 1400$ bar, the highest pressure reported). These numbers differ appreciably from pressure-induced changes obtained earlier³⁵⁾ by conductivity measurements of SDS at 35°C; presumably, there are too many assumptions made in the latter method to obtain accurate numbers. However, the trend in j vs. P is similar for both methods.^{35, 53)} If the concentration of micelles C_m is defined by the relation $C_m = (C_2 - \text{CMC})/j$, then a C_m vs. P plot will exhibit an opposite curvature to the j vs. P plot: compression first ($P < P_{\text{max}}$) yields a larger number of smaller micelles, followed by fewer and larger aggregates for $P > P_{\text{max}}$. A

comparison of the CMC (P) and $C_m(P)$ behavior is drawn.⁵³⁾ Unlike SDS, the nonionic $C_{12}E_6$ exhibits no reversal in j vs. P , but a monotonic decrease from $j \sim 325$ at 1 bar to $j \sim 200$ at 1400 bar, with jj/JP approaching zero above ~ 1000 bar for $C_{12}E_6$. This difference is attributed to oxyethylene hydration which is said to prevent micellar growth.⁵³⁾

This laboratory has employed photon correlation spectroscopy (PCS) to measure the pressure dependence of the diffusion rate of micelle particles in the presence of high salt concentrations.^{50,59)} Assuming the Stokes-Einstein equation^{1,2)} $D = kT/6\pi\eta R_h$, the average hydrodynamic radius R_h is obtained for micelles in solutions where intermicellar interactions are effectively screened at high ionic strength.⁷⁴⁻⁷⁶⁾ While the results from dynamic light scattering may be considered controversial,⁷⁷⁾ the trends observed with pressure should be meaningful. The strong promotion of micellar growth in electrolyte solutions diminishes rapidly as the temperature is raised.⁷⁸⁾ We have determined the micellar radius R_h of four cationic surfactants under pressure and found that R_h may increase, decrease or remain constant with increasing pressure until the solubility limit is exceeded and phase separation occurs at high pressures. The $R_h(P)$ functional dependence is determined by the temperature regime and the alkyl chainlength of the amphiphilic cation. Micelles shrink at lower temperatures, grow at the higher temperatures and shrink, then grow at intermediate temperatures. The pressure effect is most pronounced for CTAB, as illustrated in Fig. 4.⁵⁹⁾ It is noted that at intermediate temperatures, where micelles first shrink and then grow, the result is similar to that observed by Nishikido *et al.*⁵³⁾ for SDS. In light of the varied results on cationic

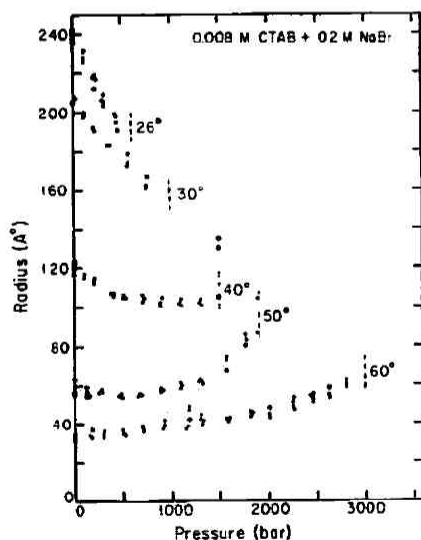


Fig. 4. Pressure dependence of the hydrodynamic radius of micelles in 0.008 M CTAB plus 0.2 M NaBr solutions at 26°, 30°, 40°, 50° and 60°C.

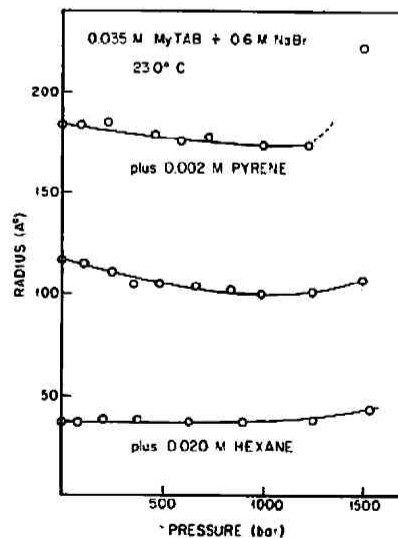


Fig. 5. Pressure dependence of the hydrodynamic radius of micelles in 0.035 M MyTAB plus 0.6 M NaBr solutions at 23.0°C (middle curve) and in the presence of pyrene (upper curve) or hexane (lower curve) solubilizates.

surfactants, it would be premature to discuss the various factors which might be responsible for a shift in the balance of hydrophobic and hydrophilic forces determining micellar size and shape.⁷⁹⁾

Solubilization is a most important phenomenon in micellar systems, and the site of solubilization as well as the structural perturbations introduced by probe molecules remains a topic of active interest.^{80,81)} Figure 5 compares the effect of pressure on the radius of MyTAB micelles in solutions of high salt concentrations with surfactant solutions which have solubilized pyrene or hexane. A probe study at 1 atm by the PCS method has recently shown⁸²⁾ that MyTAB micelles exhibit additional growth in the presence of pyrene but shrink upon addition of hexane, provided the probe/surfactant concentration ratios exceed 0.003 and 0.03, respectively. The reasons for the opposite effect on micellar size by these two solubilizates probably reflects their different site of solubilization: pyrene near the micellar surface and hexane within the micellar nucleus. What is remarkable about Fig. 5 is the absence of a stronger pressure effect on micellar size in the presence of pyrene or hexane. The apparent solubilities of the smaller micelles containing hexane are only slightly greater than in the unsolubilized micelles, while the larger micelles with adsorbed pyrene do show significant growth just prior to phase separation. If these studies are combined with other spectroscopic studies of micelles under pressure, then answers to the questions raised by Menger¹⁶⁾ about the nature of surfactant clusters in water will be more easily attained.

This review will conclude with the one report of a very different type of measurement under pressure: the kinetics of micellization.^{45,83,84)} Temperature-jump techniques are employed to measure various relaxation times τ of SDS plus electrolyte as a function of applied pressure.⁴⁶⁾ The commonly observed τ_2 attributed to stepwise monomer addition and removal showed only a small pressure sensitivity which might reflect compensating factors. However, a new relaxation time τ_3 , also in the millisecond time range, is resolved for $C_2 > 10 \times \text{CMC}$ solutions under pressure: τ_3 has a significant pressure dependence, corresponding to $\Delta V^* \sim 70 \text{ cm}^3 \text{ mol}^{-1}$. Seright, Grieger-Block and Thusius⁴⁶⁾ suggest that τ_3 may be identified with a change in micelle shape (sphere to rod). Unfortunately, this is the only technique that has so far addressed pressure effects on shape: thus, their conclusion cannot be verified by other means.

Pressure studies of surface-active agents, as sketched above, have only begun: the agenda for continuing work is large and the various subtleties of current theories of micelles should be tested with pressure experiments. Studies of micelles under pressure, although a small subject area, does combine questions of strong electrolyte solutions, water structure, and large hydrophobic assemblies—with obvious significance to biochemistry. Therefore, pressure work on surfactant systems promises greater impact in the future.

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